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PRELIMINARY INVESTIGATION INTO THE EFFECT

OF HIGH TEMPERATURE THERMAL ANNEALS CN THE

FIGURE OF MERIT OF SILICON GERMANIUM ALLOYS

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FINAL TECHNICAL REPORT

by

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UNIVERSITY OF WALES COLLEGE OF CARDIFF

PRELIMINARY INVESTIGATION INTO THE EFFECT OF HIGH TEMPERATURE THERMAL ANNEALS ON THE FIGURE OF MERIT OF SILICON GERMANIUM ALLOYS

ABSTRACT

In this report is embodied the results of a preliminary theoretical and experimental investigation into the effect of high temperature thermal anneals on the thermoelectric figure of merit of silicon germanium-gallium phosphide material.

A realistic theoretical model for the silicon germanium alloy system is employed to investigate the effect of an increase in the doping level on the electrical power factor $\alpha^2\sigma$ where α is the Seebeck coefficient and σ the electrical conductivity. The assumption is made that the addition of gallium phosphide to silicon germanium alloy serves only to increase the dopant solubility and hence the carrier concentration. The theoretical analysis indicates that the reported factor of 1.6 increase in the carrier concentration of heat treated silicon germanium-gallium phosphide material compared to conventional silicon germanium alloy would result in an increase in the electrical power factor of between 12-14% at room temperature rising to 18-22% at 1000K.

Comparison of measured transport data on silicon germanium-gallium phosphide material and a zone levelled silicon germanium alloy confirms that substantial improvements in the electrical power factor can be obtained by subjecting the silicon germanium-gallium phosphide material to high temperature thermal anneals, while the total thermal conductivity remains relatively unchanged.

Although there are differences in the increases in the power factor obtained by different researchers. The results of this programme of work support the conclusion that the electrical power factor and hence the figure of merit of silicon germanium-gallium phosphide can be significantly improved by high temperature thermal anneals.

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III   General Introduction

Silicon germanium alloys are established semiconductor material for high temperature applications and they have been successfully employed in the fabrication of thermocouples of radioisotopic powered generators which provided onboard electrical power to the Lincoln Experimental Satellites LES 8 and LES9 and the voyager spacecrafts[1]. Materials based upon the silicon germanium alloys have also been[1] chosen for use in NASA's SP-100 project in which orbiting nuclear reactor powered thermoelectric generators will produce up to 100 kilowatt of electrical power[2].

In space applications weight is a major consideration and over the past ten years or so effort have been made to reduce the weight of the thermoelectric conversion system by improving the performance of the thermocouple material. The material's performance is conveniently expressed in terms of its figure of merit $Z = \alpha^2\sigma/\lambda$ where α is the Seebeck coefficient, σ the electrical conductivity and λ the thermal conductivity. The thermal conductivity consists essentially of two parts, a lattice (phonon) contribution λ_L and an electron (hole) contribution λ_e. The lattice thermal conductivity is the major component, even in very heavily doped thermoelectric materials. Effort has focussed on improving Z and hence increasing the conversion efficiency by reducing the lattice component of the thermal conductivity. Substantial reductions in λ_L have been achieved through the use of very small grain size material[3] and through the introduction of additives such as gallium phosphide[4]. However, all published information indicates that although a reduction in λ_L can be obtained any improvement in Z is minimal due to an accompanying degradation in electrical properties – primarily a reduction in carrier mobility.

Recently attention has turned to improving the electrical power factor (EPF). It has been reported that the EPF of silicon germanium – gallium phosphide can be significantly increased by subjecting the material to high temperature anneals. This increase in the EPF is not accompanied by a significant change in the thermal conductivity and results in an improvement in the thermoelectric figure of merit[5]. A suggested mechanism responsible for the reported increase in performance is that the gallium phosphide enhances the dopant

solubility hence permitting the carrier concentration to approach closer to its optimum value[6]. These developments lead to the present programme of research.

IV   Objectives

The programme of work proceeded in two stages, the first one theoretical and the second one experimental.   In the first stage the realistic theoretical model for silicon germanium alloy, which had been developed for a previous U.S. Army contract[7] would be used to explore the potential improvement in the electrical power factor and hence thermoelectric figure of merit which accompanies an increase in dopant solubility.

The experimental programme of work involves annealing specimens of silicon germanium-gallium phosphide at high temperatures and measuring the Seebeck Coefficient and electrical conductivity. Finally an assessment would be made of the effect of high temperature anneals on the electrical power factor of silicon germanium-gallium phosphide and possible mechanisms suggested which are responsible for any observed increase in the materials performance.

V   Theoretical Programme of Work

1.   Introduction

Silicon germanium alloys cannot be described as narrow band semiconductors, however the high level of doping normally employed in thermoelectric materials necessitates the inclusion of a deviation from the usually assumed parabolic bands.   The non-parabolicity of the bands is interpreted in terms of a parameter $\beta = k_B T / E_g$ where k_B is the Baltzmann constant and T is the absolute temperature. E_g is the energy band gap.   Non-parabolicity has a strong influence on the electrical properties at high carrier concentration.   Moreover, these effects are quantitatively dependent on the scattering mechanicam.   The development of a comprehensive and realistic theoretical model which provides a description of the electrical properties of the silicon germanium alloy system is difficult and best approached in stages, commencing with a working model and progressing to more realistic models of increased complexity.

At room temperature and a little above, acoustic phonon scattering is the dominant charge carrier scattering mechanism. In the model adopted we have considered a multivallied, non parabolic band structure but excluded the effect of intervally scattering. Intervally scattering requires the presence of high energy phonons which are not excited at around room temperature

2. Theoretical model

It is convenient to work in terms of reduced electrical conductivity σ' and reduced Seebeck coefficient, α' where

$$\sigma' = \left(\frac{k_B}{e} \right)^2 \frac{T}{\lambda_L} \sigma \qquad \text{and} \qquad \alpha' = \frac{e}{k_B} \alpha$$

$$\sigma' = \left(\frac{k_B^2 h C_{11}}{3\pi^2 \epsilon_1^2} \right) N_V \; {}^0L_{-2}^1 \; \frac{T}{(m_c^* \lambda_L)}$$

$$\text{and} \qquad \alpha' = (\delta - \xi) \quad \text{with} \; \delta = ({}^1L_{-2} / {}^0L_{-2})$$

The electrical figure of merit is given by

$$\alpha^2 \sigma = \frac{\lambda_L}{T} \; \alpha'^2 \sigma' = \left(\frac{k_B^2 h C_{11}}{3\pi^2 \epsilon_1^2} \right) \frac{N_V}{m_c^*} \; {}^0L_{-2}^1 \; (\delta - \xi)^2$$

with ϵ_1 the accoustic deformation potential, C_{11} the longitudinal elastic constant N_V the number of equivalent energy valleys, m_c^* the conductivity (intertial effective mass) and λ_L the lattice thermal conductivity. The generalised Fermi integrals ${}^nL_\ell^m$ which appears in the electronic transport coefficient expressions are given by:

$$^nL_\ell^m (\xi) = \int_0^\infty \left(- \frac{\partial f}{\partial \eta} \right) \eta^n \, [\eta(1 + \beta\eta)]^m \, (1 + 2\beta\eta)^\ell \, d\eta$$

f is the Fermi distribution function, $\eta = E/kT$, $\beta = k_B T/E_g$

The carrier concentration n_c is related to the Fermi level by:

$$n_c = N_V \frac{1}{3\pi^2} (2m_{ds}^* k_B T)^{3/2} \; {}^0L_0^{3/2}$$

The density of states $g_s(E)$ of a single valley is given by:

$$g_s(E) = 4\pi \left(\frac{2m^*_{ds}}{h^2} \right)^{3/2} E^{\frac{1}{2}} dE$$

where E is the carrier energy measured with respect to the band edge and m^*_{ds} is the density of states effective mass for a single valley.

If there are N_v equivalent valleys, the total density of states $g_t(E)$ is given by:

$$g_t(E) = N_v(g_s(E)$$

This can then be incorporated in our model by defining a total density of states effective mass m^*_{dt} such that

$$g_t(E) = 4\pi \left(\frac{2m^*_{dt}}{h^2} \right)^{3/2} E^{\frac{1}{2}} dE$$

This gives $m^*_{dt} = N_v^{2/3} m^*_{ds} = N_v^{2/3}(m_1 m_2 m_3)^{1/3}$

where m_1, m_2 and m_3 are the components of the mass tensor along the principal axis.

The effective mass values for the electronic states in the alloys are about the same as for corresponding states in pure crystals, consequently initially a simple linear compositional dependence of the effective mass was employed using effective mass values given in Table 1, making no distinction between the density of states and conductivity effective masses.

	Ge	Si
m_t/m_o	0.08	0.19
m_L/m_o	1.58	0.92
m_d/m_o	0.216	0.32
m_c/m_o	0.117	0.26

Table 1 - Effective mass values

The values for C_{11} and E_1 are taken to be 1.7×10^{11} Nm^{-2} and 6.2eV respectively. The calculations have been carried out for 70% and 90% silicon in view of the expected usefulness of silicon rich

alloys in actual device applications. A slight improvement in the model can be obtained by considering the density of states and conductively effective masses separately for silicon and germanium and obtaining the corresponding values for the alloy composition by linear interpolations.

3. Theoretical Results

In the theoretical analysis it is assumed that the normal material doping level is well below the maximum required to optimise the figure of merit and that no significant changes in the effective mass on the other band structure parameters of silicon germanium alloy accompany the addition of gallium phosphide. The theoretical Z versus carrier concentration curve remains unaltered as shown schematically in Figure 1. With the carrier concentration n_1 being determined by the solubility limit of the dopant. The addition of gallium phosphide enables the carrier concentration to increase to a value n_2 which approaches closer to the maximum of the Z versus carrier concentration curve. The theoretical model described in section V. 2. has been employed in obtaining the dependence of the electrical power factor on carrier concentration for different alloy compositions at room temperature (Figure 2) and at 1000K (Figure 3). Using Figures 2 and 3 it is possible to estimate the increase in the electrical power factor which corresponds to the factor of 1.6 increase in carrier concentration measured at 500°C, which accompanies high temperature anneals[6].

The results are presented in Tables 2 and 3.

Composition (%Si)	Carrier Concentration (cm^{-3})	E.P.F. (W/mK^2)	% increase in E.P.F.
70	10^{19}	40×10^{-3}	
	1.6×10^{19}	45×10^{-3}	12.5
90	10^{19}	35×10^{3}	
	1.6×10^{19}	40×10^{3}	14.3

Table 2. Theoretical increase in the electrical power factor at room temperature.

Composition (%Si)	Carrier Concentration (cm^{-3})	E.P.F. (W/mK^2)	% increase in E.P.F.
10	3×10^{19}	22×10^{-3}	
	5×10^{19}	26×10^{-3}	18
90	3×10^{19}	18×10^{-3}	
	5×10^{19}	22×10^{-3}	22

Table 3. Theoretical increase in the electrical power factor at 1000K.

V. Discussion

The theoretical increase in the electrical power factor which accompanies an increase in the carrier concentration by a factor of 1.6 range from 12-14% at room temperature rising to 18-22% at 1000K. At 500 C this increase is about half the reported value of 42%. This simple model which assumes that the addition of GaP only causes an increase in the dopant solubility is unable to account for the reported increase in the electrical power factor. Either the measured increase is incorrect or the theoretical model requires refining to take into account changes in band structure and density of states which may accompany the addition of GaP to silicon germanium alloy.

VI. Experimental Work

1. Introduction

The thermoelectric properties of heavily doped silicon germanium alloys are notoriously dependent upon the history of the material[8] and the same is probably true for silicon germanium-gallium phosphide. Considerable differences in the magnitude in the increase in the electrical power factor, which accompanies high temperature anneals, have been reported by different laboratories[6]. Evidently additional experimental data on these materials is required and this prompted the following limited programme of experimental work.

2. Procedure

Thermoelectric transport property measurements were made on a sample of silicon germanium-gallium phosphide material obtained from the Jet Propulsion Laboratories, Pasadena. An ingot shaped specimen 2mm x 2mm x 6mm was cut from a pressed pellet. Its density measured using Archemedes principle was 2.95 $gmcm^{-3}$. X-ray analysis indicated that the alloy composition was about $Si_{85}Ge_{15}$. The specimen was head treated in air at 1500K for two hours and air quenched. It was subsequently heated in air at lower temperatures in the range 1400K to 1100K. The heat treatment was periodically interrupted by quenching the specimen in air to room temperature. An oxide layer which formed on the specimen only after the initial high temperature anneal was removed with HF(40%).
Prior to measurements the surface of the specimen was polished and washed in distrilled water. Electrical resistivity and Seebeck coefficient measurements were made from room temperature to about 830K.

3. Results

The measured Seebeck coefficient and electrical resistivity for a silicon germanium-gallium phosphide specimen are presented in Figure 4, 5 and 6. In Figure 7 are displayed the electrical power factors as measured at different laboratories together with measurements made some time agao at Cardiff on a zone levelled specimen of silicon-germanium alloy obtained from the David Sarnoff Centre (RCA).

4. Discussion

The silicon germanium-gallium phosphide alloy which had been subjected to a high temperature thermal anneal exhibited an increased electrical figure of merit compared to standard silicon germanium materials. At the highest temperature of measurement i.e. about 830K the increase in the electrical power factor was . This compared favourably with the results reported by TECO but was considerably less than the increase reported by JPL.

VII General Discussion and Conclusions

The experimental results obtained support the proposition that the electrical power factor can be significantly increased by subjecting silicon germanium-gallium phosphide material to high temperature thermal anneals. The measurements, although only undertaken on one sample indicates that the percentage increase in electrical power factor is somewhat less than that obtained at the Jet Propulsion Laboratory and about the same order as reported by TECO. A theoretical analysis based upon a realistic model for silicon germanium in which it is assumed that the presence of gallium phosphide serves only to increase the solubility of the dopant, would account for this level of improvement. However, the model adopted is unable to explain the much greater improvement reported by workers at JPL.

VIII Acknowledgements

Dr. C. M. Bhandari is thanked for acting as consultant to the project and his valuable contributions to the work embodied in this report are appreciated. Dr's. C. Wood and J. W. Vandersande are thanked for providing the silicon-germanium allium phosphide material, and Dr. Gao Min for measuring the electrical power factor. Finally Mrs. J. Phillips is thanked for typing the report.

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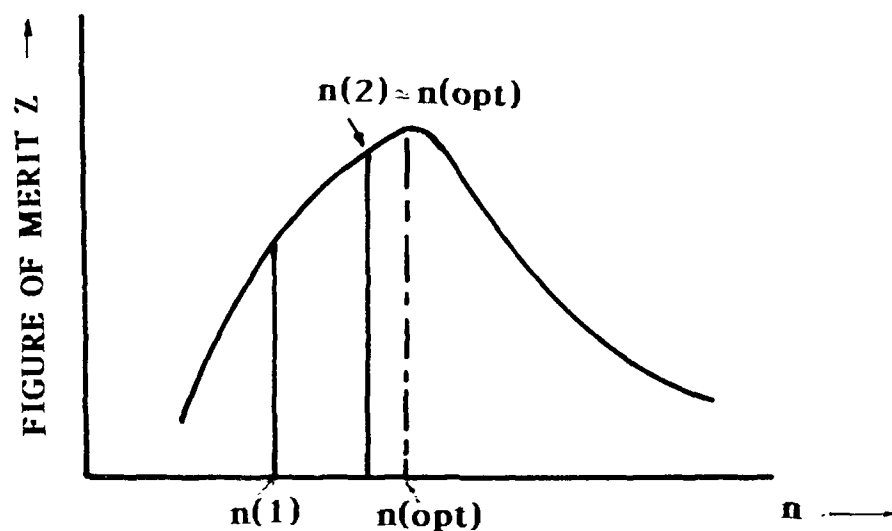
FIG.1(a) FIGURE OF MERIT versus n (schematic).
SIMPLE MODEL: NO BAND STRUCTURE CHANGES WITH
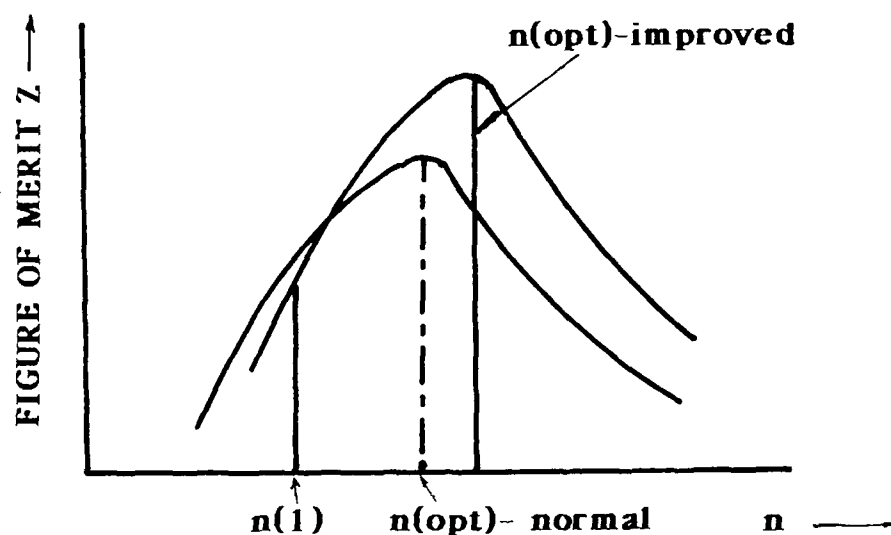GaP DOPING : ONLY SOLUBILITY INCREASE.

FIG.1(b) FIGURE OF MERIT versus n (schematic).
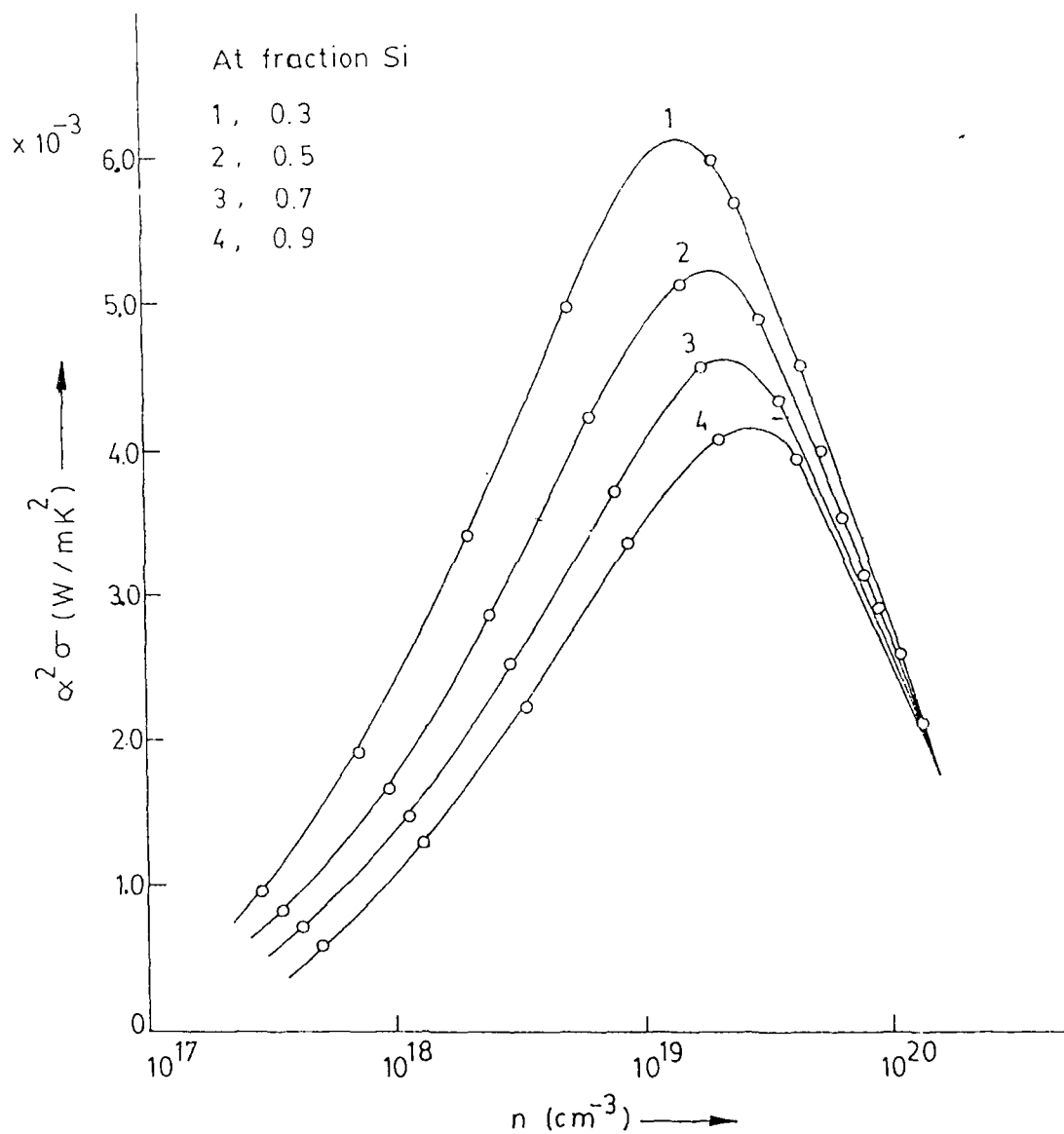IMPROVED MODEL:BAND STRUCTURE CHANGES
ACCOMPANY SOLUBILITY INCREASE.

At fraction Si
1 , 0.3
2 , 0.5
3 , 0.7
4 , 0.9

$\times 10^{-3}$

$\alpha^2 \sigma \ (W/mK^2) \longrightarrow$

$n \ (cm^{-3}) \longrightarrow$

FIG.2   THEORETICAL PLOT OF ELECTRICAL POWER FACTOR versus CARRIER CONCENTRATION AT 300K.
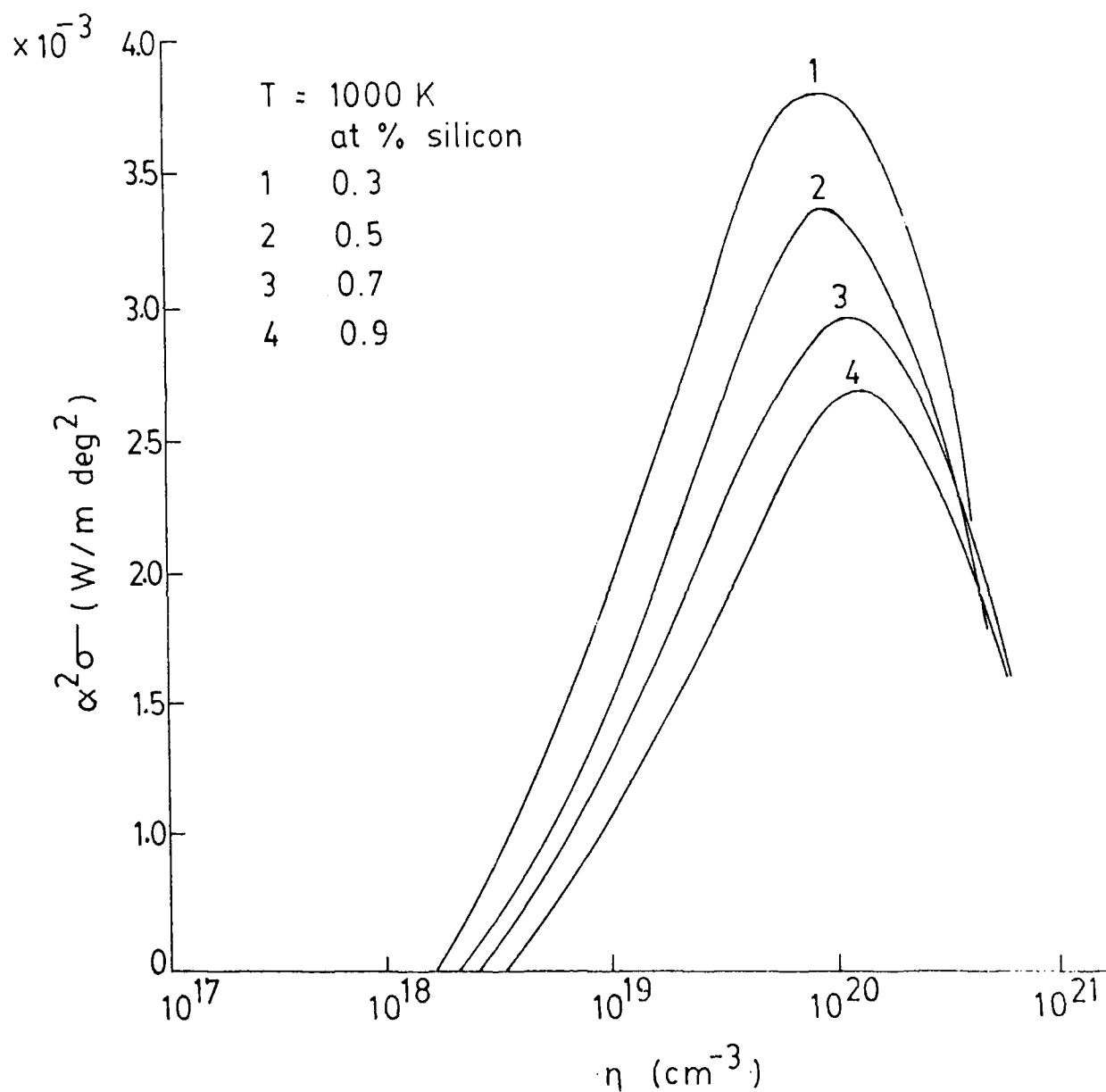
FIG.3 THEORETICAL PLOT OF ELECTRICAL POWER
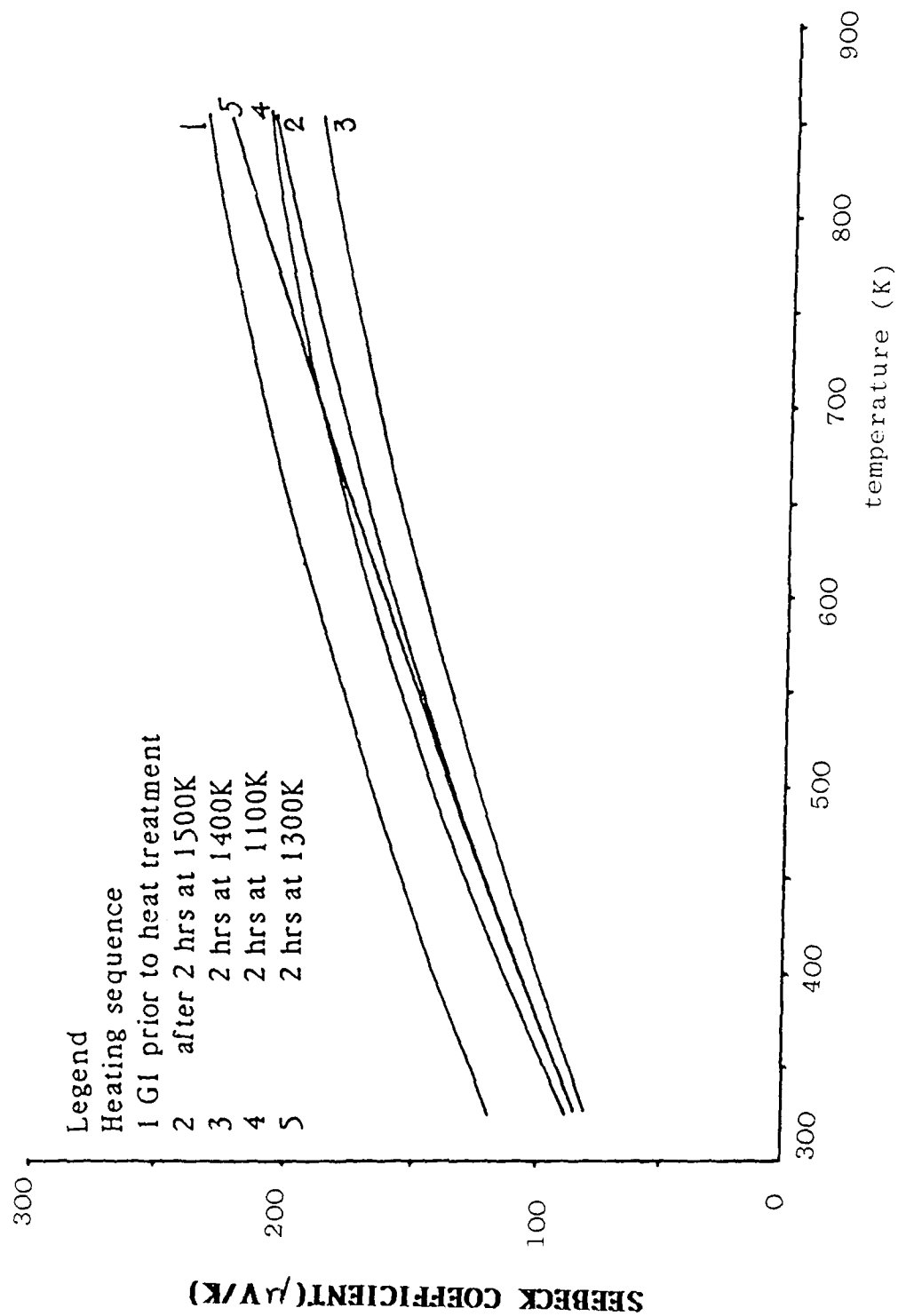FACTOR versus CARRIER CONCENTRATION AT 1000K.

Legend
Heating sequence
1 G1 prior to heat treatment
2   after 2 hrs at 1500K
3   2 hrs at 1400K
4   2 hrs at 1100K
5   2 hrs at 1300K

FIG.4 SEEBECK COEFFICIENT versus TEMPERATURE

SEEBECK COEFFICIENT(μV/K)

temperature (K)

300 400 500 600 700 800 900

0   100   200   300

Legend
Heating sequence
1 G1 prior to heat treatment
2   after 2 hrs at 1500K
3   2 hrs at 1400K
4   2 hrs at 1100K
5   2 hrs at 1300K

FIG.5 ELECTRICAL RESISTIVITY versus TEMPERATURE.

Legend
Heating sequence
1 GI prior to heat treatment
  after 2 hrs at 1500K
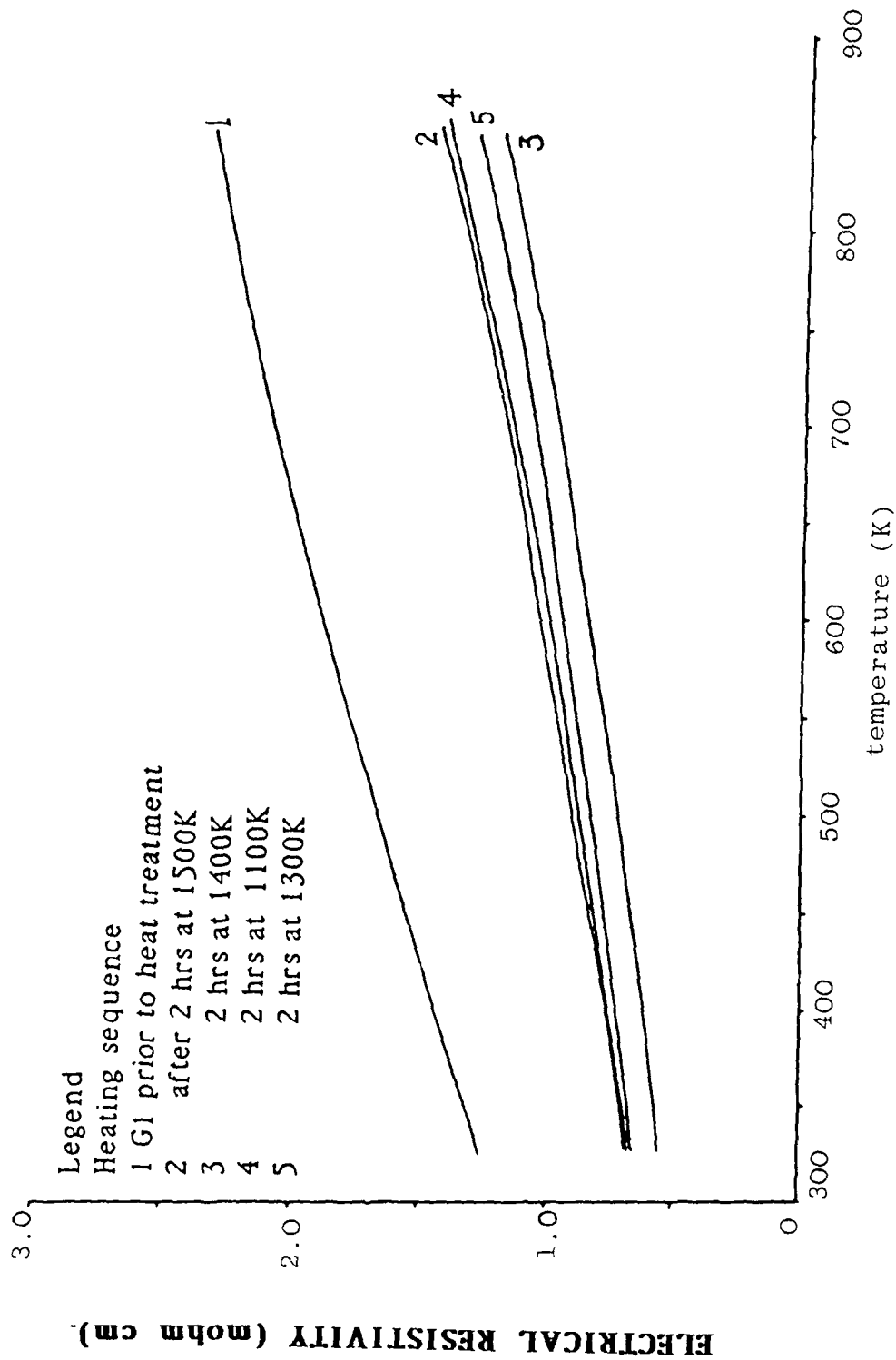2   2 hrs at 1400K
3   2 hrs at 1100K
4   2 hrs at 1300K
5

ELECTRICAL POWER FACTOR (μW/K cm).
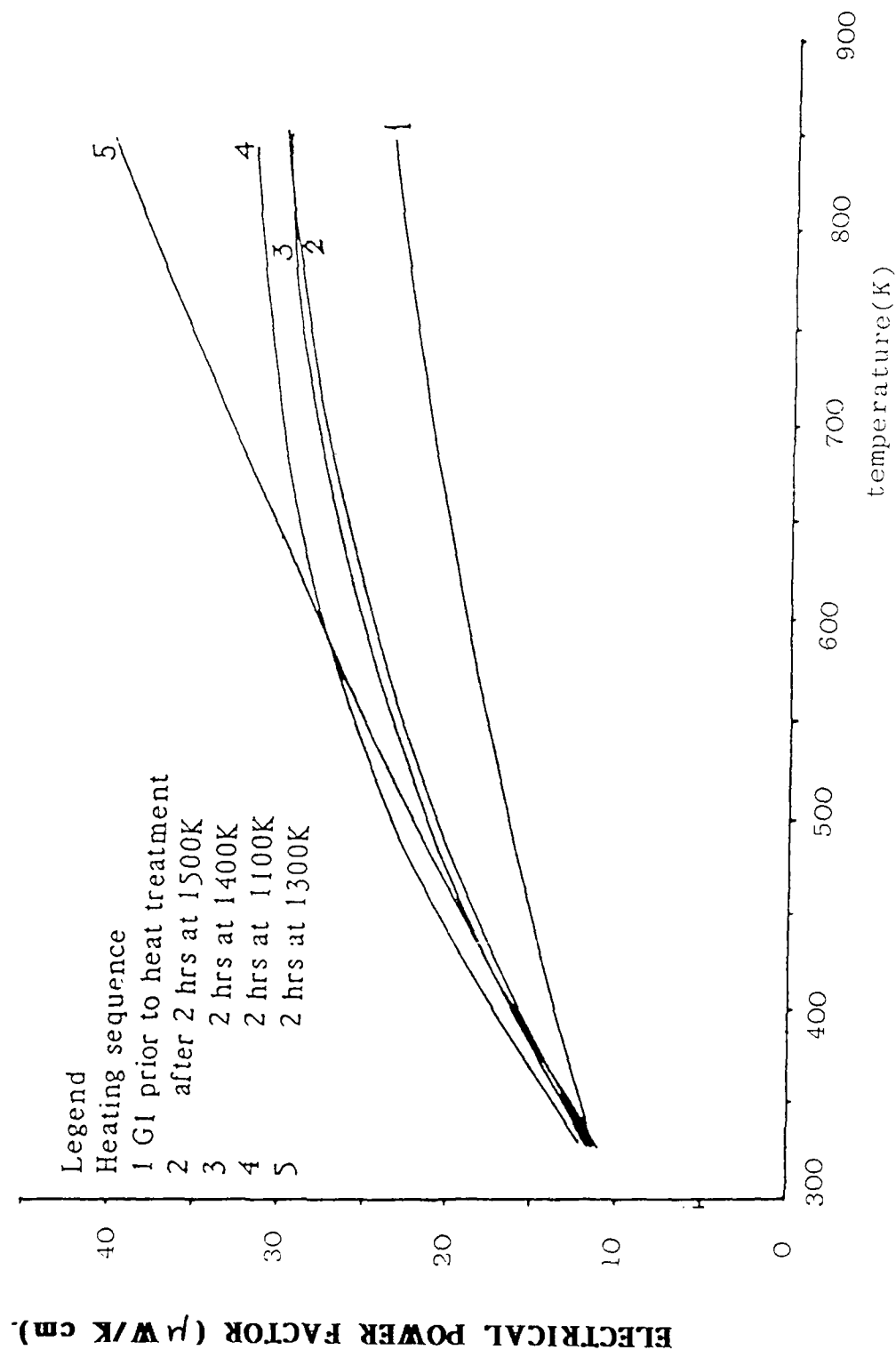
temperature(K)

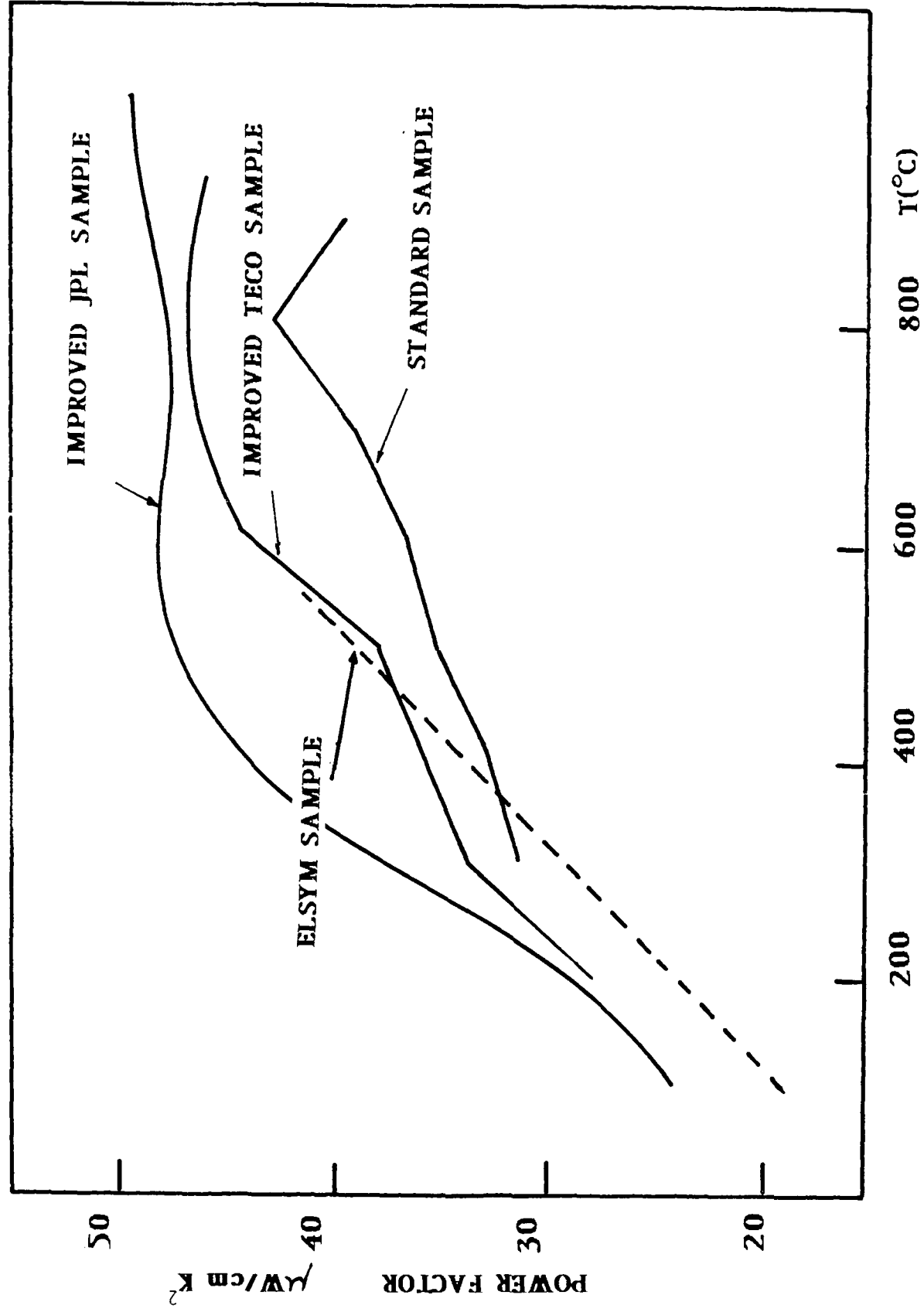FIG.6 ELECTRICAL POWER FACTOR versus TEMPERATURE.

FIG 7. COMPARISON OF THE ELECTRICAL POWER FACTOR
DATA ON SiGe-GaP AS A FUNCTION OF TEMPERATURE